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Phase transitions in block copolymers resulting in a discontinuous change of the spatial period of mesophases

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Abstract. – The phase behavior of a melt of two-scale multiblock copolymers has been theoretically studied in the framework of the Weak Segregation Limit theory with a two-component order parameter. The existence of a thermodynamically stable mesophase with two scales of the space periodicity has been revealed for a melt of monodisperse nonperiodic heteropolymers. For the first time a discontinuous change with temperature of the spatial period of the mesophases has been predicted.

Among the systems dealt with by soft-matter physics of prime importance are solutions and melts of block copolymers whose linear macromolecules consist of rather long blocks of single-type monomeric units [1,2]. A distinctive feature of the phase behavior of such systems is their ability to form spatially periodic mesophases with the periods lying in the nanometer scale [3,4]. Essentially, by varying the architecture of block copolymers' macromolecules, it is possible to obtain under the same conditions mesophases of different morphology [3,5–7]. The thermodynamic behavior of heteropolymer liquids of such a type is successfully described by the self-consistent field theory based on the solution of nonlinear parabolic partial differential equations. In the framework of this theory, analytic results can be obtained only in two limiting cases, namely, Weak Segregation Limit (WSL) and Strong Segregation Limit (SSL). In this paper we will apply the first of these, which rests on the ideas of the Landau theory of phase transitions [8]. Leibler [9] was the first who invoked the WSL theory to describe the phase behavior of an incompressible melt of monodisperse diblock copolymers. The phase diagrams constructed by him for macromolecules of different length and chemical composition comprise regions of the existence of three mesophases, *i.e.*, Body-Centered Cubic (BCC),

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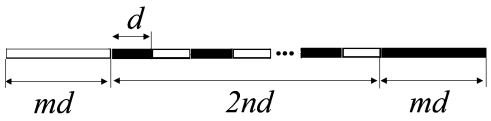

Fig. 1 – Molecular architecture of a block copolymer macromolecule considered earlier [12, 13]. Rectangles of different colors correspond to the blocks of chemically different monomeric units.

Hexagonal (HEX) and Lamellar (LAM). These classical mesophases, as well as the Gyroid mesophase found later [10], were long believed to be the only possible in melts of binary block copolymers [11]. However, recently the authors of papers [12,13], studying the phase behavior of melts of binary linear block copolymers with the two-scale architecture (fig. 1), predicted in the framework of the WSL theory the possibility of the thermodynamic stability of a number of other mesophases, such as Simple Cubic, Face-Centered Cubic and that known as BCC2. The reason for the appearance of these non-classical mesophases is a strong angular dependence of the vertex functions of the Landau free energy describing these block copolymers. A specific feature of the melts of such two-scale macromolecules is that their structure factor $S(q)$ can have two maxima (fig. 2) associated with two branches of the nontrivial spinodal for some values of the parameters characterizing the chemical structure of these copolymers [14]. Of particular interest are Double Spinodal Points (DSPs) belonging to both such branches since at these points the loss of absolute thermodynamic stability of the spatially homogeneous state occurs simultaneously for wave vectors of two different lengths. Because of this, there are serious reasons to expect the emergence of thermodynamically stable mesophases characterized by two spatial periodicity scales in the vicinity of a DSP line. Obviously, the phase diagrams presented in papers [12,13] do not claim to be correct in this area for the values of the structure characterizing parameters m and n (see fig. 1) located within the white region in fig. 2. This is because the traditional approach of the WSL theory with one-component order parameter employed in these papers in principle excludes two-scale mesophases from consideration.

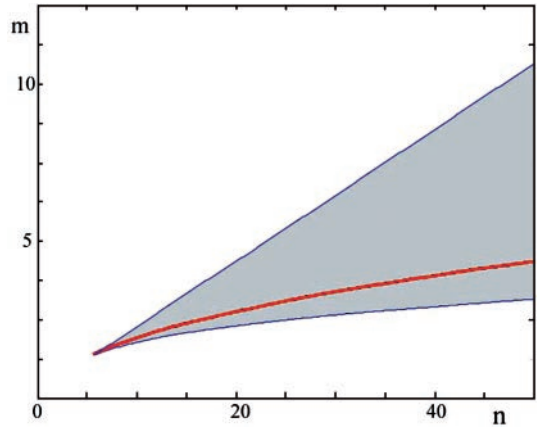

Fig. 2 – Classification diagram of the structure factor $S(q)$ for a melt of the block copolymer whose architecture is schematically depicted in fig. 1. The function $S(q)$ has one and two maxima in the white and gray areas, respectively. For the values of the parameters m and n located on the heavy (DSP) line the heights of both maxima are equal.

One of the central problems of the WSL theory consists in deriving expressions that relate the coefficients of the amplitude expansion of the Landau free energy with the vertex functions. The first to present such expressions for three particular two-scale mesophases was Nap [15]. Later a diagram algorithm was suggested [16] enabling one to write down analogous expressions for any mesophase with two scales of spatial periodicity. Using this algorithm to consider a melt of two-scale *periodical* macromolecules the authors [17] managed to reveal for the first time the possibility of the existence in the phase diagram of a region of thermodynamic stability of some two-scale mesophases. The present work aims at exploring the possibilities of the existence of such mesophases in an incompressible melt of *nonperiodic* macromolecules of a monodisperse block copolymer with the architecture depicted in fig. 1. That is why we, contrary to the authors of papers [12, 13], will be particularly concerned with the region of the values of parameters m and n, lying in the vicinity of the DSP line (fig. 2).

In the context of the WSL theory, the Landau free-energy functional looks in the momentum representation as follows [7]:

$$\mathcal{F} = \sum_{l=2}^{4} \frac{1}{l!} \sum_{\{\boldsymbol{q}_i\}} \tilde{\Gamma}^{(l)}\left(\boldsymbol{q}_1, \ldots, \boldsymbol{q}_l\right) \delta_{\mathrm{K}} \left(\sum_{j=1}^{l} \boldsymbol{q}_j \right) \prod_{s=1}^{l} \tilde{\psi}(\boldsymbol{q}_s), \tag{1}$$

where $\delta_{\mathrm{K}}(\boldsymbol{q})$ is the Kronecker delta and $\tilde{\psi}(\boldsymbol{q})$ represents the Fourier transform of the order parameter $\psi(\boldsymbol{r})$. Vertex functions $\tilde{\Gamma}^{(3)}$ and $\tilde{\Gamma}^{(4)}$ are controlled exclusively by the parameters of the chemical structure of a macromolecule, whereas $\tilde{\Gamma}^{(2)}(q) = S^{-1}(q) - 2\chi$ depends additionally on temperature through the Flory parameter χ [7]. By virtue of the architecture symmetry of the macromolecules under consideration, the function $\tilde{\Gamma}^{(3)}$ vanishes identically at all values of its arguments. Hence, the disorder-order transition occurring on the spinodal is always a second-order phase transition [8]. Only such phase transitions were predicted earlier [12, 13] for the macromolecules depicted in fig. 1.

Minimizing functional (1), it is possible to find the Fourier transforms of the equilibrium densities of monomeric units of different types. This, particularly, provides a possibility to specify the spatial symmetry group of an equilibrium mesophase. When constructing a phase diagram, the consideration is usually restricted to a set of several candidate mesophases choosing the one which possesses the minimal value of the free energy.

In the vicinity of the DSP line (fig. 2), it is natural to introduce a two-component order parameter which in the first-harmonic approximation will read [16, 17]

$$\begin{aligned} \tilde{\psi}(\boldsymbol{q}) = {} & \frac{A}{\sqrt{k}} \sum_{j_1=1}^{k_1} \left[e^{i\varphi_{j_1}} \delta_{\mathrm{K}} \left(\boldsymbol{q} - \boldsymbol{q}_{j_1}^{(\mathrm{L})} \right) + e^{-i\varphi_{j_1}} \delta_{\mathrm{K}} \left(\boldsymbol{q} + \boldsymbol{q}_{j_1}^{(\mathrm{L})} \right) \right] + \\ & + \frac{B}{\sqrt{k}} \sum_{j_2=1}^{k_2} \left[e^{i\varphi_{j_2}} \delta_{\mathrm{K}} \left(\boldsymbol{q} - \boldsymbol{q}_{j_2}^{(\mathrm{S})} \right) + e^{-i\varphi_{j_2}} \delta_{\mathrm{K}} \left(\boldsymbol{q} + \boldsymbol{q}_{j_2}^{(\mathrm{S})} \right) \right]. \end{aligned} \tag{2}$$

The summation in the first and the second sums in the right-hand part of this expression is up to k_1 and $k_2 = k - k_1$ values of subscripts of wave vectors $\{\boldsymbol{q}_{j_1}^{(\mathrm{L})}\}$ and $\{\boldsymbol{q}_{j_2}^{(\mathrm{S})}\}$ of the first harmonic set [16] of the mesophase under consideration. The values of moduli q_{L} and q_{S} of the above-mentioned vectors are determined by minimization of the amplitude expansion of the Landau free energy

$$F = \nu_1 \tau_1 A^2 + \nu_2 \tau_2 B^2 + \beta_1 A^4 + \beta_A A^3 B + 2\beta_{12} A^2 B^2 + \beta_B A B^3 + \beta_2 B^4 \tag{3}$$

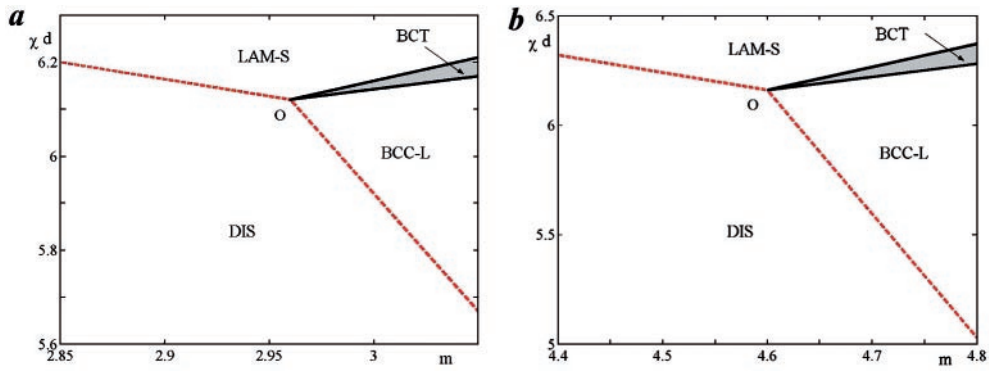

Fig. 3 – Morphology diagrams for a melt of the block copolymer schematically depicted in fig. 1 at $n = 15$ (a) and $n = 50$ (b). Firm and dashed curves correspond to the first and the second phase transitions' lines, respectively. The two-scale BCT mesophase is stable in the shaded region only. The coordinates of the point O in (a) and (b) are equal to (2.96, 6.12) (a) and (4.60, 6.16) (b). The slopes of the firm lines are equal to 0.56, 0.99 (a) and 0.60, 1.05 (b), while the slopes of the dashed lines are equal to $-5.00, -0.73$ (a) and $-5.65, -0.80$ (b).

obtained by means of the substitution of expression (2) into formula (1). Here the following designations are employed:

$$\tau_\alpha = (\chi_\alpha - \chi)\, d, \qquad 2\chi_\alpha d = S^{-1}(q_\alpha), \qquad \nu_\alpha = k\,/k_\alpha \qquad (\alpha = \mathrm{L}, \mathrm{S})\,. \tag{4}$$

The absence of cubic terms in expansion (3) is due to the architecture symmetry of the macromolecules, while the terms proportional to A^3B and AB^3 are present only under the description of the deformed FCCs with $r = 1, 4$ [16] among all candidate mesophases considered in this paper. We calculated their free energy with allowance for the above-mentioned additional terms. At fixed values of the chemical structure parameters m and n, the values of the coefficients β_1, β_2, β_{12}, β_A, β_B for a given mesophase are functions of values q_L and q_S only. The values of these latter near the DSP line will just slightly differ from q^*_L and q^*_S, respectively, at which the function $S(q)$ attains its maximum. This difference will be the less, the closer point (m, n) is to the DSP line where equalities $q_\mathrm{L} = q^*_\mathrm{L}$ and $q_\mathrm{S} = q^*_\mathrm{S}$ hold exactly.

Having considered all two-scale mesophases among those which are characterized by the two-component order parameter (2) [16], we constructed in the vicinity of the DSP line the morphology diagrams presented in fig. 3. It should be emphasized that since m, unlike the temperature (*i.e.*, parameter χ), is not a thermodynamic parameter, these diagrams are not, strictly speaking, true phase diagrams [18]. These latter are obtained from a morphology diagram as its one-dimensional cross-sections at fixed values of parameter m.

As is clear from the diagram in fig. 3a, four lines of phase transitions spring from point O. The vertical line passing through point O represents the phase diagram of a system with parameters m and n situated on the DSP line. Analogous lines for values $m < 2.96$ and $m > 2.96$ represent phase diagrams of systems whose parameters lie in the vicinity of the DSP line in fig. 2, below and above it, respectively. Systems of the first type only undergo a phase transition from the Disordered state into a lamellar mesophase (LAM-S) with small period $\sim 1\,/q^*_\mathrm{S}$. Qualitatively different is the appearance of the phase diagram of the second type system, where the primary phase transition on the spinodal will be followed at decreasing temperature by two secondary first-order transitions. The first of these goes from a BCC mesophase (BCC-L) with large period $\sim 1\,/q^*_\mathrm{L}$ into a two-scale Body-Centered Tetragonal (BCT) mesophase, whereas the second transition transforms this BCT mesophase into a LAM-S mesophase.

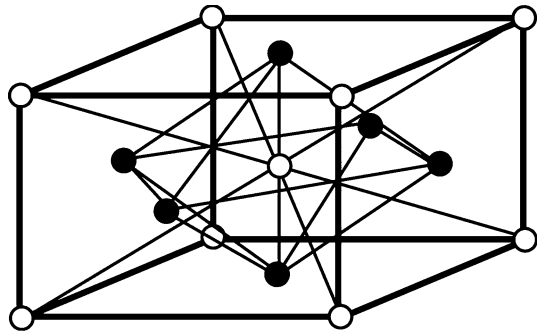

Fig. 4 – Positions of maxima (open circles) and minima (full circles) of the order parameter $\psi(\boldsymbol{r})$ in the Bravais cell of the BCT mesophase. On every thin line connecting two maxima or two minima the saddle point of this function is located.

The spatial symmetry of the periodic function $\psi(\boldsymbol{r})$ of an arbitrary mesophase can be unambiguously characterized by specifying the location of its extremal points in the three-dimensional Euclidean space. Following this idea the spatial configuration of field $\psi(\boldsymbol{r})$ describing BCT mesophase is illustrated in fig. 4. The positions of maxima and minima of this field form a parallelepiped and a deformed octahedron, respectively.

Essentially, a secondary transition in melts of architecturally symmetric block copolymers is in principle impossible to predict in the framework of the WSL theory with one-component order parameter [8]. The secondary transitions revealed by us result not only in the change of the spatial symmetry of the mesophases but also in a discontinuous change at the transition point of the scales of their space periodicity. This is just the matter of the fundamental distinction of these secondary transitions from those proceeding in all non-symmetric block copolymer systems examined earlier (see, for instance, [9, 13]) in the course of which the period of mesophases remains the same. Noteworthy, a change in the period of a mesophase for decreasing temperature takes place also in melts of polydisperse multiblock copolymers described by the WSL theory with one-component order parameter [19–21]. However, in such systems this change proceeds continuously.

Inspection of fig. 3a shows that the ratio κ of the intervals of values χ, corresponding to the existence of BCT and BCC-L mesophases, is relatively small and equal to 0.08. This means that with a slight temperature change it is possible to realize a switch of the phase state from BCC-L to LAM-S mesophase, whose periods differ by a factor of 3.25. Increasing the number of small blocks n, one can make the difference between the periods of switched mesophases considerably more pronounced. For example, for $n = 50$ (fig. 3b) this ratio equals 7.36, whereas the κ value turns out to be equal to 0.07.

Morphology diagrams, presented in fig. 3 are built with allowance for three assumptions whose validity was verified by us:

1) *Amplitudes A and B of the components of the order parameter* (2) *should be small enough.* In our case, the highest possible values of these amplitudes do not exceed 0.02.

2) *Absence of the contributions from the second harmonics into the Landau free energy.* This property has been proved by us for LAM-S and BCC-L mesophases for all points of the morphology diagrams, depicted in fig. 3. It can be expected that the above-mentioned property remains true for the BCT mesophase as well.

3) *Smallness of quantities* $\delta q_\alpha = |q_\alpha - q_\alpha^*| / q_\alpha^*$, *ensuring the fairness of the employment of values* q_α *instead of* q_α^* *when finding the periods of the two-scale mesophases at hand.* The highest values of these quantities do not exceed one per cent at all points in fig. 3.

Therefore, in this work the possibility of the existence of two-scale mesophase in a melt of nonperiodic multiblock copolymer has been established for the first time. Besides, the conditions have been predicted under which varying the temperature within narrow limits, one may induce a pronounced change in the period of a mesophase. It can be expected that such a discontinuous switch will be of considerable practical consequence.

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